

# Live-Fire Range Sustainment

## Energetic Materials as Environmental Contaminants

JANNAF  
31<sup>st</sup> Propellant Development and  
Characterization Subcommittee  
20<sup>th</sup> Safety and Environmental  
Protection Subcommittee  
25-27 March 2003

Judith C. Pennington, PhD  
U.S. Army Engineer Research  
and Development Center  
Environmental Laboratory  
Vicksburg, MS

## The Challenge

**Military readiness** is imperative



**Environmental stewardship**  
is imperative

**Tools needed to integrate the two are limited.  
The database upon which to develop those  
tools is also limited.**

# Military Readiness

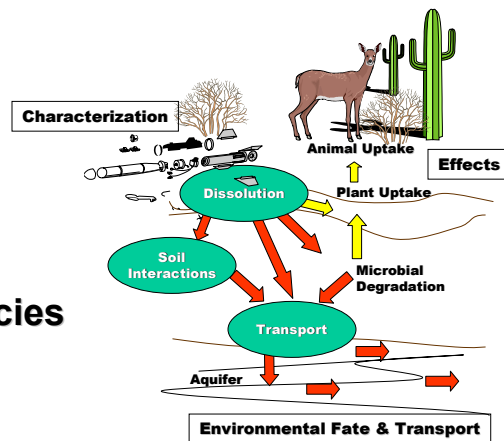
- Training Range Activities (HE)
  - Artillery/Mortar
  - Antitank rocket range
  - Tank firing range (Battleruns)
  - Hand grenades
  - Multi-Use ranges
  - Air to ground bombing/missiles
  - Ground to air missiles
  - Demolition/“blow-in-place”
  - Mines
  - Naval munitions
- Weapon Systems Testing



3

# Environmental Stewardship

- Ground water
- Soil
- Ecosystems
- Threatened and endangered species
- Public health



4

# Origins of Explosives in the Environment

- Manufacturing of explosives
- “Load-and-Pack” operations, filling munitions with explosives
- Live-fire soldier training
- Weapon systems testing
- Demolition of munitions/UXO
- Demilitarization of munitions
- Commercial enterprises



5

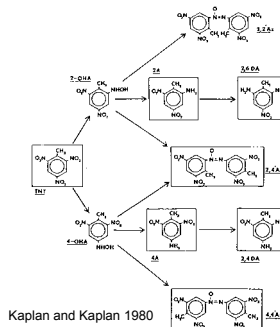
# Contaminants of Concern

- **TNT**
- **RDX**
- **HMX**
- **DNTs**
- **Tetryl**
- **Ammonium picrate**
- **White phosphorus**
- **Others**
  - **Perchlorate**
  - Nitroglycerin
  - PETN
  - Degradation and transformation products
  - Components of smokes, obscurants, pyrotechnics
  - Heavy metals
  - Related organic compounds

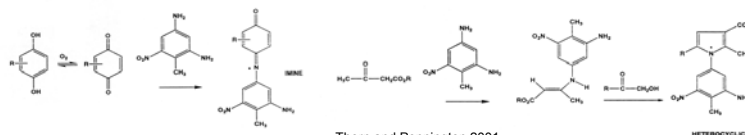
6

## TNT Transport/Degradation

- Transformation products are common when TNT is present
- **Attenuation by soils is significant**
- Transport occurs when volume of soluble contamination exceed capacity of soil to attenuate, e.g., manufacturing sites



NONHYDROLYZABLE BONDS

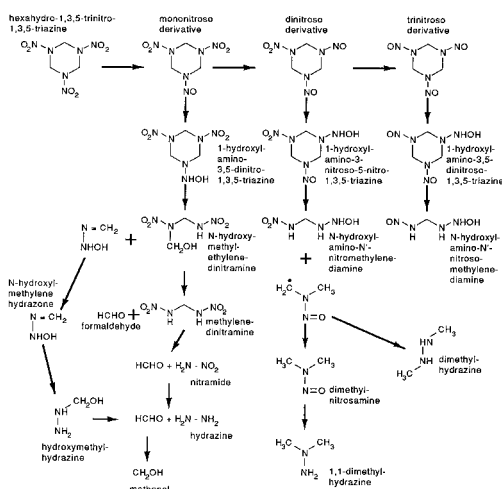


Thorn and Pennington 2001

HETEROGENEOUS

## RDX Transport/Degradation

- Mineralization is minimal in the vadose zone, but enhanced under anaerobic conditions
- Some transformation products are undesirable
- Readily transported from soil to ground water
- RDX is readily taken up by some vegetation

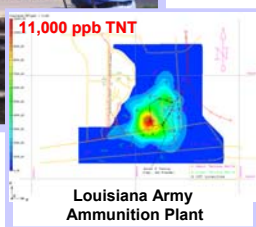
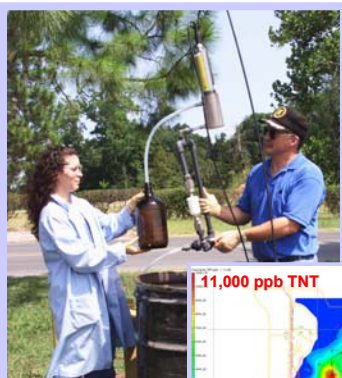


McCormick, Feeherry, and Levinson 1976

8

# Status of Explosives Contamination

## Manufacture and load-and-pack sites

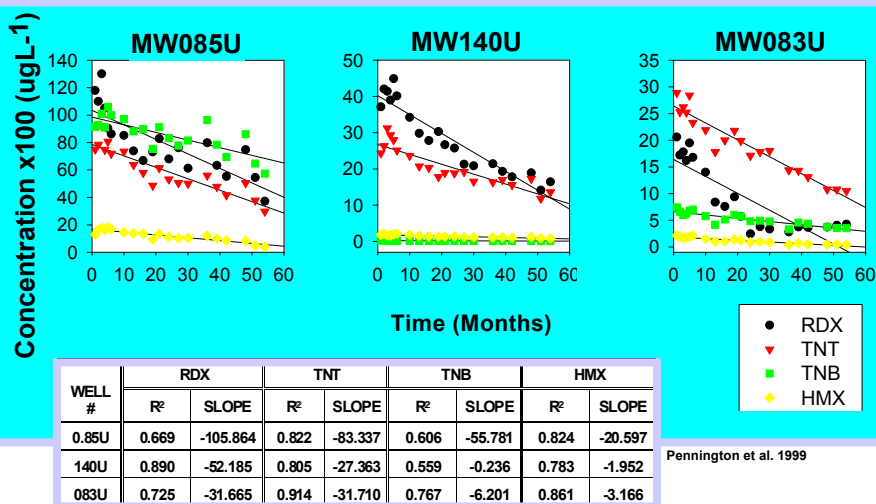


- Focus of clean-up efforts since early 1980s
- Most heavily contaminated soils and ground water have been treated, or are currently under treatment
  - Incineration • Composting
  - Pump-and-treat • In situ
  - Monitored natural attenuation
- Point sources; originally aqueous

9

## Manufacturing Site

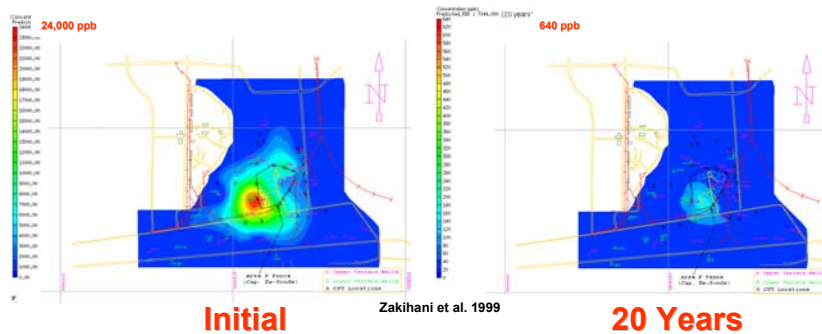
### Concentrations in LAAP Ground Water Over Time



10

# Manufacturing Site: LAAP

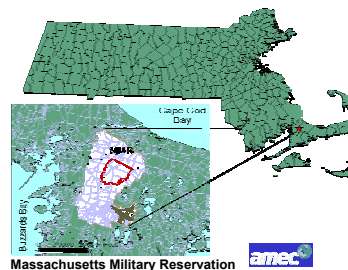
## Ground Water Model RDX Plume



11

## Massachusetts Military Reservation

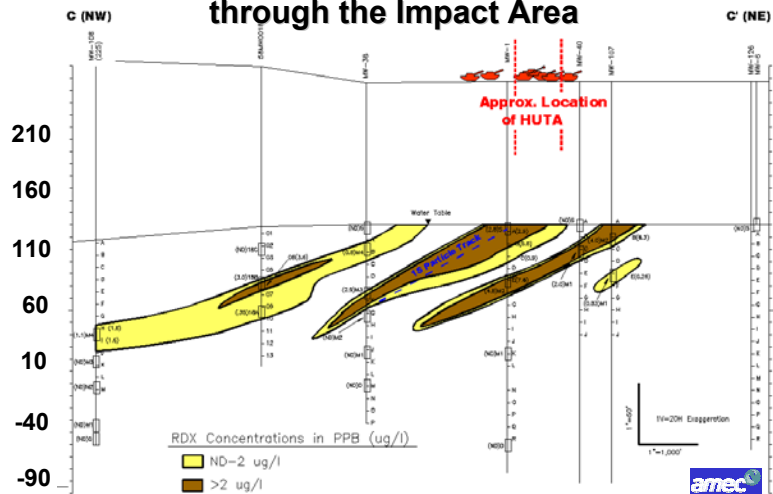
- 21,000-acre facility located on Cape Cod, MA
- Approximately 14,000 acres of Training Range and Impact Area
- Sits on the Cape Cod Aquifer, a sole source of drinking water for 148,000 permanent and 425,000 seasonal residents
- Soil is highly permeable
- Groundwater exceedance of the Lifetime Health Advisory of 2 ppb for RDX and TNT (one site)
- Soil contaminants include concentrations (ppm) up to
  - 43 RDX, 10 HMX, 17 2,4DNT, 130 nitroglycerin, transformation products of TNT, other organics, and metals
- EPA Order (1997) required
  - **Suspension of training**
  - Elimination of current and potential sources to aquifer
  - Monitoring plan to assess compliance
  - Restoration of areas disturbed by the action



12

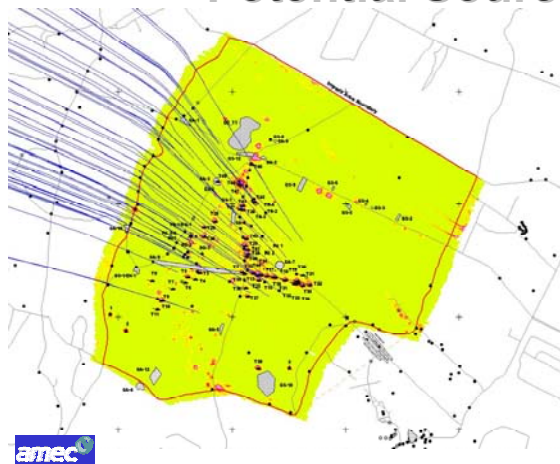
# RDX Plumes at MMR

## Longitudinal Cross-Section through the Impact Area



13

## MMR Central Impact Area Potential Sources



- High-order detonations
- Low-order detonations
- Ruptured UXO
- OB/OD sites

14



# Massachusetts Military Reservation



- **Investigations for Ground Water Study Program (1997-2002)**
  - 2,041 profile samples from 171 soil borings
  - 1,014 wipe samples from UXO
  - 3,495 ground water profile samples from 256 borings
  - 5,233 groundwater samples from 651 monitoring wells at 256 locations
  - 56 documents in 2002 alone
- **Ground water contamination**
  - Three source locations: Central Impact Area, Demolition Area 1, and J Range
  - Contaminants of Concern: RDX, HMX, 4ADNT, 2ADNT, TNT, 2,4DNT, perchlorate
- **Ongoing activities**
  - Hydraulic containment at Demolition Area
  - Feasibility Study for Central Impact Area
  - Update of regional ground water model
  - Evaluation of UXO as ground water contamination source
  - Further characterization of J Ranges and other selected sites

15

## Distribution and Fate of Energetics on DoD Test and Training Ranges SERDP Project CP1155



- **Range characterization**
  - Sampling of residues on active ranges
- **Defining residues from controlled detonations**
  - High-order detonations on snow
  - Blow-in-place on snow
  - Controlled low-order detonations
- **Residues at firing points**



16

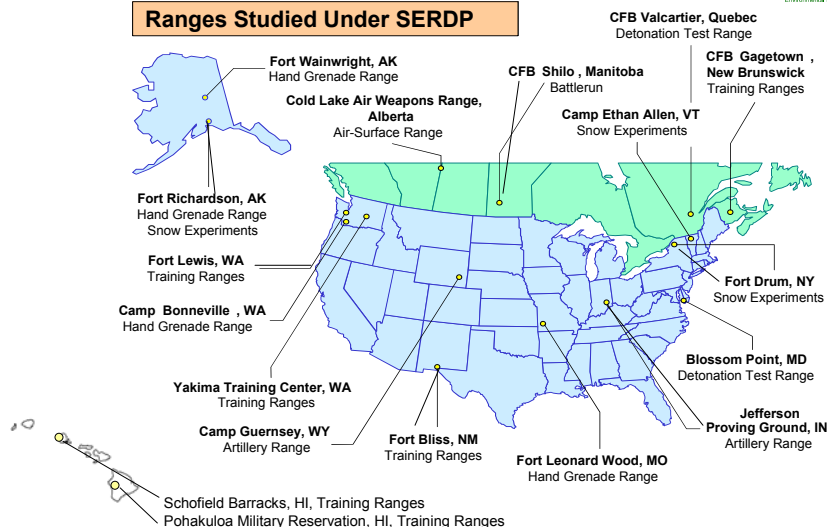


# Distribution and Fate of Energetics on DoD Test and Training Ranges

## SERDP Project CP1155



### Ranges Studied Under SERDP



17

# Residue Deposition from Operational Use of Munitions



<u>Munition</u>	<u>RDY (grams)</u>	
	<u>Mass in item</u>	<u>Residue</u>
M67 hand grenade	110	0.000025
105-mm howitzer	1,300	0.000100
81-mm mortar	560	0.001000
60-mm mortar	220	0.000074
40-mm grenade	19	0.001600
120-mm mortar	1,800	0.004100

Jenkins/CRREL 2002



18

# Soil Concentrations Near Low-Order Items (Ft. Bliss)



<u>Munition</u>	<u>Concentration (µg/kg)</u>	
	<u>RDX</u>	<u>TNT</u>
155-mm	not detected	2,520,000
155-mm	not detected	8,590,000
155-mm	1,780	722,000
37-mm	not detected	1,220
2.75" rocket	1,130,000	13,500
90-mm	678,000	1,110,000

Jenkins/CRREL 2002



Explosive chunks recovered from soil surface

Low-order hand grenade with Comp B chunk inside

Low-order 155-mm projectile with scattered chunks

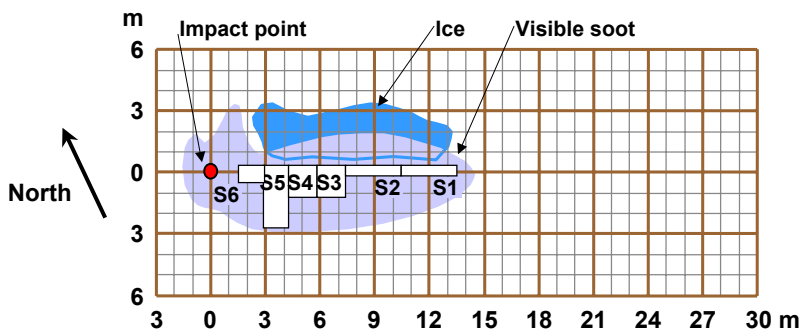
## Estimation of Residues from Detonations on Snow (ug)

<u>Munitions</u>	<u>RDX</u>	<u>TNT</u>	<u>HMX</u>
M67 Hand Grenade	26	<1	<1
81-mm Mortar (C4)	35,000	240	8,000
C4 Alone	61,000	<1	26,000
M19 Anti-Tank Mine (C4)	280	<1	860
M15 Anti-Tank Mine (C4)	4,000	8	410
60-mm Mortar (Point Detonation)	630	18	8
60-mm Mortar (Proximity)	72	14	19
120-mm Mortar (Point Detonation)	4,000	320	140

Jenkins/CRREL 2002



## Estimation of Residues from 60-mm Mortar Fired onto Snow

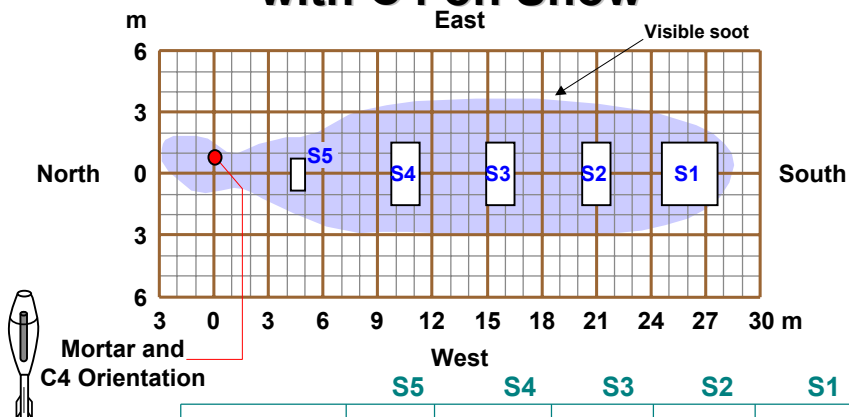


	S6	S5	S4	S3	S2	S1
<b>RDX (<math>\mu\text{g}/\text{m}^2</math>)</b>	0.60	6.13	0.88	0.33	0.32	0.35
<b>NG (<math>\mu\text{g}/\text{m}^2</math>)</b>	< d	0.01	< d	< d	< d	< d

Jenkins/CRREL 2002

21

## Estimation of Residues from Detonations of 81-mm mortar with C4 on Snow



	S5	S4	S3	S2	S1
<b>RDX (<math>\mu\text{g}/\text{m}^2</math>)</b>	12.4	5.2	4.3	1.6	1.0
<b>NG (<math>\mu\text{g}/\text{m}^2</math>)</b>	802	1,530	367	119	124
<b>TNT (<math>\mu\text{g}/\text{m}^2</math>)</b>	0.06	< d	< d	0.05	< d <sub>22</sub>

Jenkins/CRREL 2002

# Estimating Residues from Controlled Low-Order Detonations



- 60- and 81-mm mortars
- 105- and 155-mm artillery projectiles



Setting up controlled low-order detonations



Low-order fragments



Residue from controlled low-order detonations



Witness plates and tarp for controlled low-order detonations



Residue analysis from controlled low-order detonations



TNT chunks from controlled low-order detonations

23

# Residues at Firing Points



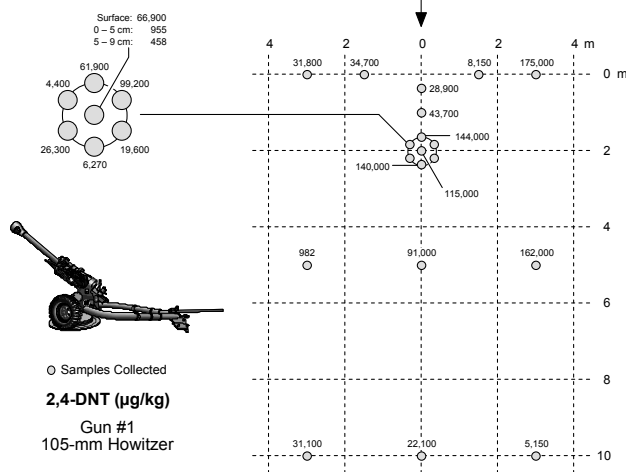
Propellant residues can be significant at firing points  
of heavy artillery



105-mm Howitzer

24

# Residues at Firing Points Heavy Artillery



Jenkins-049

25

# Residues at Firing Points

Certain rockets can deposit a continuous trail of residues from firing point to impact and behind the gun



26



# Residues at Firing Points

Perchlorate is a potential contaminant of concern for certain rockets

Titans on the Space Shuttle



- Likely to be common on ranges
- No regulatory limits are set; however, may be imminent
- Regulatory limits may be in the low ppb range (e.g. 1 ppb)
- May also be a problem in BIP (e.g., spotting charge in low-impact training rounds, or LITR)

27

## Status of Explosives Contamination

Live-fire training  
and weapon systems testing ranges

- Massachusetts Military Reservation (MMR) 

- SERDP Project CP1155 

- Characterization

- Fate and Transport

- Environmental Effects

- Challenges

- What we know

- Future directions



# Range Characterization/Remediation Challenges of Source and Scale



Expansive size



Extreme spatial heterogeneity



Diverse uses over time



Variable munitions performance  
low-order



Blow-in-place practices



Various climates  
29

## Characterization What we know

- **Distribution of explosives residues**
  - Random sampling is least effective
  - Integrated sampling approaches are needed
- **Sample handling/analysis**
  - Efficient compositing and subsampling techniques are critical
  - Chemical detection limits must be low for adequate characterization
- **Characteristics of residuals are specific to range firing activities**





# Characterization

## What we know



Concentrations of residues from high-order detonation are limited

Low-order detonations are significant point sources of contamination



TNT chunks

Firing points as well as impact points can become contaminated

31

# Characterization

## What we know



*Blow-in-place* demolition of UXO can contribute significant contamination

Climate can exert significant effects on the character of residues



32

# Characterization

## What we know

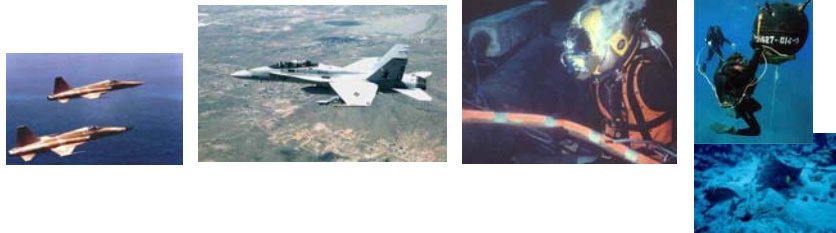
- RDX is a significant contaminant of concern on live-fire ranges
- TNT poses less threat to ground water than RDX
- Propellant residues at firing points can be significant

33

# Characterization

## Future Directions

**Characterize air force and naval ranges**



**Continue characterization  
of residues at firing points**



34

# Characterization Future Directions

## Refine estimates of residues from low-order detonations



Setting up controlled  
low-order detonations



Residue from  
controlled low-order  
detonations



Witness plates and tarp  
for controlled low-order  
detonations



Residue analysis from  
controlled low-order detonations

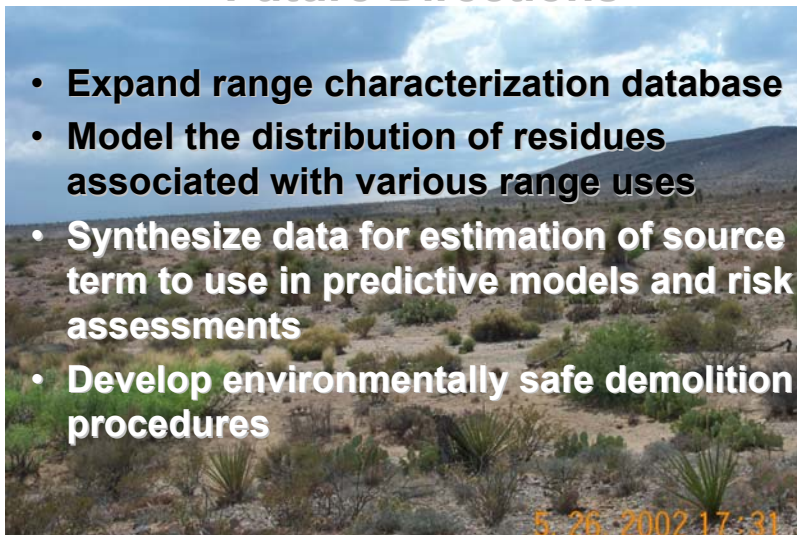


TNT chunks from controlled  
low-order detonations

35

# Characterization Future Directions

- Expand range characterization database
- Model the distribution of residues associated with various range uses
- Synthesize data for estimation of source term to use in predictive models and risk assessments
- Develop environmentally safe demolition procedures

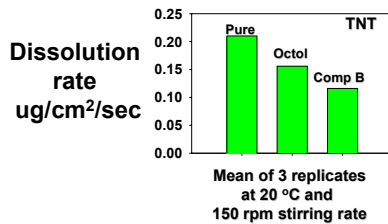


5.26.2002 17:31

36

# Fate and Transport Challenges

- Corrosion rate
  - Munitions casings
  - Safety
  - Explosives residues



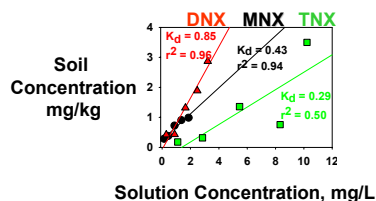
- Dissolution rate
  - Compositions

**Octol**  
70% HMX, 30% TNT  
**Comp B**  
59.5 % RDX, 39.5% TNT, 1% wax

37

# Fate and Transport Challenges

- Transport
  - Various soil/climatic settings
  - Marine environments
  - Degradation products



- Interactions with soils  
and marine sediments
  - Soil adsorption and desorption
  - Transformation
  - Degradation

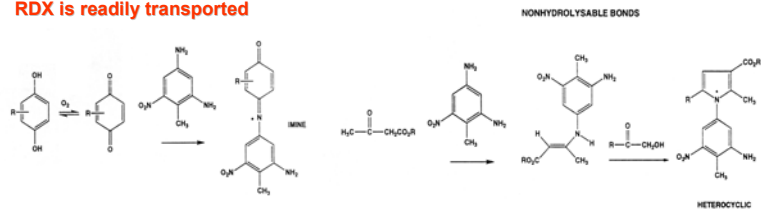
38

# Fate and Transport

## What we know

### • Soil interactions

- **Initial release** from compositions in soils tends to be **locally very high**, approaching temperature dependent saturation
- Soil **adsorption will not significantly limit transport**
- Compositions **dissolve more slowly** than individual components
- **Transformation is slow** and limited except for TNT, which transforms readily to mono amino products
- **TNT transport is limited by covalent bonding** of transformation products to soils
- Explosives residues are **resistant to microbial degradation** under conditions typical of ranges
- **RDX is readily transported**



39

# Fate and Transport

## What we know

### • Corrosion

- Corrosion rates in most environments are slow
- Casings on many high-load munitions are thick
- Some UXOs have been in place for extended time periods

### • Climate/Hydrogeology

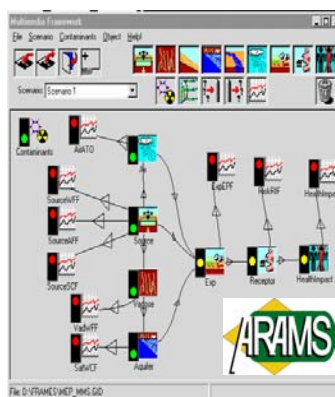
- TNT residues degrades via photolysis
- RDX is the explosive of greatest concern in ground water



40

# Fate and Transport Future Challenges

- **Process descriptors needed**
  - Propellants
  - Smokes and obscurants
- **Characterizing corrosion on bottom of UXOs**
- **Significance of non-HE organics**
- **Spatial models of the source term**
- **Transport models**
- **New generation explosives**



41

## Effects What we know

- **Toxicity varies with species (data are limited)**
- **Mono amino transformation products of TNT are typically more toxic than TNT**
- **RDX is readily bioaccumulated by plants**
- **TNT is rarely translocated from roots**



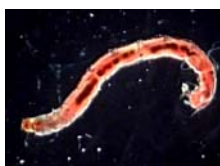
42



# Effects

## Future challenges

- Modeling exposure
- Defining representative receptor species for testing
- Filling data gaps for munitions compositions, explosives degradation products, and new generation explosives



Insect larva  
*Chironomus tentans*



Amphipod  
*Hyalella azteca*



Fathead minnow  
*Pimephales promelas*

43

## Challenges Unique to Live-Fire Training Ranges

### What to monitor:

- Number of rounds fired and locations (*How much contamination is/will be out there?*)
- Number of low-order detonations (*How do you monitor these "hot spots"?*)
- Contamination in soils resulting from low-order detonations (*Where?*)
- Contamination in soils resulting from firing point residues (*Where?*)
- Contamination in ground water resulting from range activities (*Where do you put the wells?*)
- Contamination of air
- Contamination of surface water
- Ecological impacts (*What species are sentinel? In which regions of the country?*)

### How to monitor:

- Access to
  - Ranges
  - Contaminated soils (*finding it*)
  - Contaminated ground water
  - Receptors
- Sustaining monitoring systems
  - Stability against blasts
  - Stability against range fires
  - Safety
- Scale and heterogeneity
  - Representativeness
- Release of data
  - Sensitivity levels
  - Whose data are they?

44



# Managing the Problem

- **Synthesis**
  - Environmentally “harmless” residues
  - “Trackable” residues
  - “Self-destructing” residues
- **Range Practices**
  - Tracking duds and low-order detonations
  - Removing/remediating duds and low-order detonations
  - Tracking firing positions for characterization and remediation
  - Improving blow-in-place procedures
  - Managing range use to minimized residues

45

## The direct approach to cleanup



46